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Synthesis and electronic properties of conjugated polymers based on rhenium or ruthenium dipyridophenazine complexes

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Two series of luminescent conjugated polymers based on rhenium(I) or ruthenium(II) dipyridophenazine complexes have been synthesized by the palladium catalyzed coupling reaction using divinylbenzene and aromatic dibromides as the monomers. From the photoluminescence spectra, an energy transfer process between the conjugated backbone and the metal complexes is proposed. The ruthenium containing polymers were fabricated into light emitting devices because of their better film forming qualities. The electroluminescence (EL) of the polymers originated from the emission due to the π^*–π or π^*-d transitions. Depending on the metal complex content, the polymers exhibit different absorption and EL spectra. The devices exhibit a turn-on voltage of 10 V and external quantum efficiency of 0.6%. From the cyclic voltammetry results, an additional oxidation couple was observed after the incorporation of the ruthenium complex which may contribute to the charge transport process. This was further supported by the charge mobilities measurement in which the electron and hole mobilities of the polymers are enhanced by the metal complex and are of the order of 10^{-4} cm^2 V^{-1} s^{-1}.

Introduction

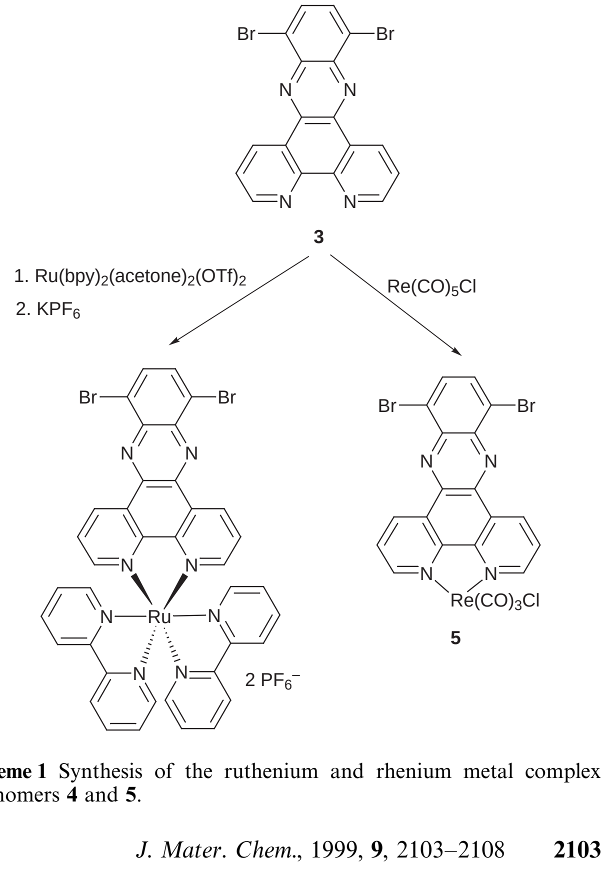
Polymeric electroluminescent devices have been gaining more attention since the first report of electroluminescence (EL) in poly(*p*-phenylenevinylene) (PPV) and its derivatives.[1–5] Organic polymers offer considerable advantages over molecular systems in device processing. Large area display devices are feasible since polymer films can be prepared by casting or spin coating. In addition, polymers usually have higher glass transition temperatures and better mechanical properties. Several examples of EL devices based on a variety of materials including conjugated polymers[6,7] and fluorescent dye-doped polymeric systems[8,9] have been reported. Recently there have been reports of employing transition or rare-earth metal complexes in EL devices.[10–12] The use of metal complexes in EL devices has the advantages of flexibility in structure design and modification. Fine tuning of the light emitting properties can be achieved by modifying the structure of the ligand or by using different transition metals. We have recently shown that the incorporation of some ruthenium complexes into the polymer main chain can enhance the charge mobility of the resulting polymer–metal complexes,[13–15] which is very important to the performance of EL devices.

The chemistry and photophysics of ruthenium polypyridine complexes have been studied extensively.[16,17] They exhibit relatively long lived metal-to-ligand charge transfer (MLCT) transitions which make it a promising candidate for EL devices. Here, we report the light emitting and charge transport properties of a series of novel conjugated polymers which consist of a PPV mainchain incorporated with different proportions of quinoxaline-5,8-diyl (monomer **6**) and dipyridophenazine complexes of ruthenium or rhenium (monomers **4** or **5**). Some physical properties such as charge carrier drift mobilities and luminescence properties were studied by different techniques. They were found to exhibit interesting luminescence properties and modest carrier mobilities. This paper reports the results.

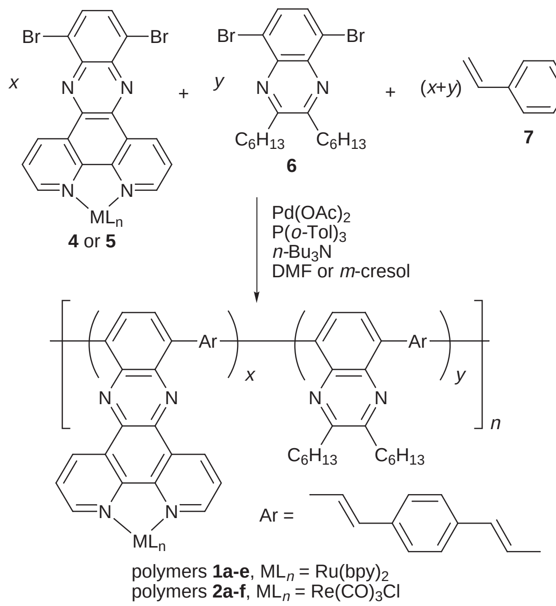
Results and discussion

Synthesis of polymers

Both series of polymers, **1a–e** and **2a–f** were obtained in good yield by using the palladium catalyzed Heck coupling reaction. The inherent vicosities of all polymers are in the range 0.2–0.4 dL g^{-1}. Some of their properties are summarized in Table 1. The palladium catalyzed reactions are proved to be a versatile



Scheme 1 Synthesis of the ruthenium and rhenium metal complex monomers **4** and **5**.



Scheme 2 Synthesis of polymers.

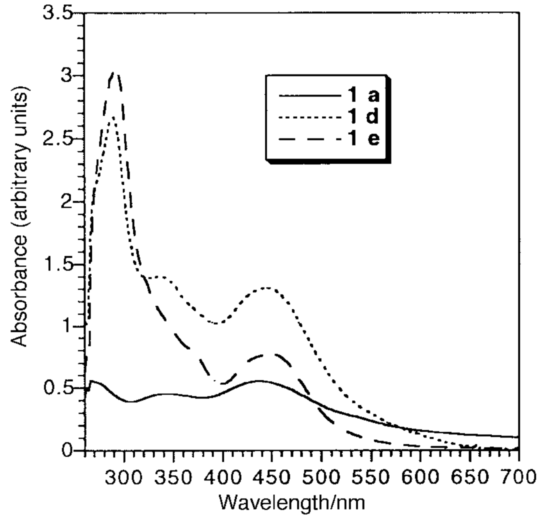


Fig. 1 UV–VIS absorption spectra of some ruthenium containing polymers in DMF solution.

Table 1 Synthesis and charge transport properties of the metal-containing polymers

Polymer	x	y	Yield (%)[a]	T_d/ °C[b]	η_{inh}/ dL g^{-1}[c]	μ_h/ cm^2 V^{-1} s^{-1}[d]	μ_e/ cm^2 V^{-1} s^{-1}[e]
1a	0	1	87	457	0.41	5.5×10^{-5}	8.5×10^{-5}
1b	0.2	0.8	61	291	0.46	4.6×10^{-5}	1.2×10^{-4}
1c	0.4	0.6	64	296	0.31	8.9×10^{-5}	1.6×10^{-4}
1d	0.5	0.5	87	309	0.31	8.7×10^{-5}	1.7×10^{-4}
1e	1	0	79	310	0.25	3.2×10^{-4}	4.0×10^{-4}
2a	0.1	0.9	56	442	0.31	—	—
2b	0.2	0.8	62	443	0.28	—	—
2c	0.3	0.7	63	408	0.31	—	—
2d	0.5	0.5	70	404	0.33	—	—
2e	0.6	0.4	53	405	0.21	—	—
2f	1	0	63	420	0.19	—	–

[a] Yield after purification by washing with methanol for 2 days. [b] Onset temperature of decomposition determined by TGA under N_2. [c] The inherent viscosity of polymer **1a** was measured in formic acid solution at 30 °C with concentration $c=0.25$ g dL^{-1}. For polymers **1b–e** they were measured in NMP while for polymers **2a–f** they were measured in *m*-cresol solution. [d] Hole carrier mobility measured at $E=40$ kV cm^{-1}. The charge mobilities of polymers **2a–f** were not determined due to poor film quality. [e] Electron carrier mobility measured at $E=40$ kV cm^{-1}.

approach in the synthesis of functional conjugated polymers as many kinds of electrophilic or oxophilic functional groups are able to survive in these reaction conditions.[18] Polymers containing a ruthenium complex (**1b**–**e**) are soluble in polar aprotic organic solvents such as *N*-methylpyrrolidinone (NMP), *N*,*N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) due to the presence of a positively charged metal complex in the polymer main chain. The metal free polymer **1a** is soluble in 1,1,2,2-tetrachloroethane and organic acids such as formic acid and trifluoroacetic acid. Optical quality films for physical characterizations can be prepared by spin coating or solution casting on indium-tin-oxide (ITO) glass slide. For the rhenium containing polymers **2a–f**, they are only soluble in *m*-cresol and slightly soluble in chloroform and tetrachloroethane. Due to the high boiling point of *m*-cresol, the films obtained by casting had poor qualities which are not suitable for device fabrication. We therefore only studied the spectral properties of the polymers in solution. Detailed physical characterizations were only carried out for polymers **1a–e**.

Structural characterizations

In the proton NMR spectra, polymer **1a** shows very broad peaks at $\delta=0.9$, 1.4, 1.6, 2.1, and 3.4 ppm due to the aliphatic hexyl group. Besides, resonant signals due to the aromatic and vinylene protons are also observed at $\delta=7.5$, 7.7, 8.1 and 8.4 ppm, while the latter one is assigned to the protons in the quinoxaline unit. After incorporation of the ruthenium complex, additional resonance signals due to the 2,2′-bipyridyl moieties are observed. By comparing the integration of the peaks due to the hexyl groups and bipyridyl units, the content of ruthenium complex can be estimated. From the FTIR spectra, the C=N stretching bands for the quinoxaline and pyridine moieties are found at 1460 and 1600 cm^{-1}, respectively. Two strong absorption bands are also found at 836 and 969 cm^{-1} which correspond to the 1,4-disubstituted phenylene and out-of-plane bending of the *trans* vinylene group, respectively. For all rhenium containing polymers **2a–f**, three very strong CO stretching bands at 2023, 1921, and 1900 cm^{-1} are observed. These are consistent with the *fac* configuration at the rhenium center. From the thermal gravimetric analysis results, all ruthenium containing polymers **1b–e** have similar values of decomposition temperature (T_d) in the range between 290–310 °C, while polymer **1a** is more stable with $T_d=457$ °C (Table 1). This indicates that decomposition starts at the metal complex when the polymer is heated to high temperatures. The rhenium containing polymers are more stable with $T_d=400$–440 °C and the metal content has little effect on the decomposition temperature.

The UV–VIS absorption spectra of the ruthenium and rhenium containing polymers are shown in Fig. 1 and 2. All

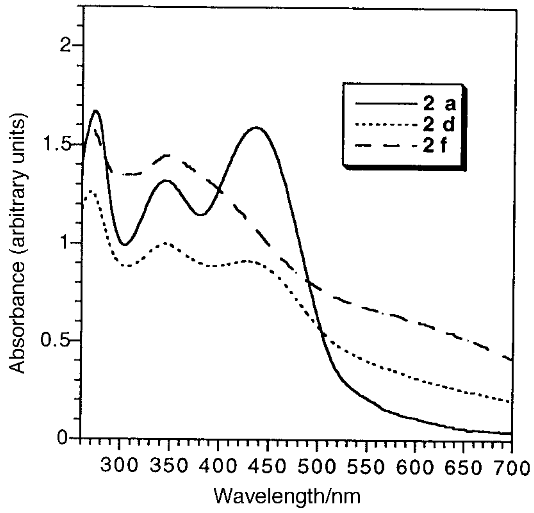


Fig. 2 UV–VIS absorption spectra of some rhenium containing polymers in *m*-cresol solution.

ruthenium polypyridine complexes exhibit a characteristic MLCT transition in the vicinity of 450–550 nm. This can be considered as the promotion of an electron from the dπ (Ru) to the π* (diimine) orbitals. From our previous report, it was found that the characteristic d–π* MLCT transition band in this type of ruthenium complex is located at *ca.* 450 nm.[19] This transition band overlaps with the π–π* transitions of the PPV conjugated backbone. On the other hand, polymers **1b–e** exhibit a very intense absorption peak at 290 nm assignable to the ligand centered (LC) transitions of the 2,2′-bipyridine moiety. The intensities of these transition bands correlate to the metal complex content in the polymers. For the rhenium containing polymers, those with low rhenium content exhibit similar main chain absorption peaks at 440 nm. The MLCT band appears as a shoulder at *ca.* 550–600 nm (Fig. 2). When the rhenium content is increased, the absorption edge of the polymers extends beyond 700 nm. In polymer **2f**, the intensity of MLCT band is comparable to the main chain absorption, which only appears as a shoulder.

The effect of changing the metal complex content can be investigated by studying their photoluminescence (PL) spectra. Polymer **1a** exhibits an emission peak centered at 560 nm due to the π*–π transitions of the conjugate main chain (Fig. 3). When the ruthenium content is increased, both the π*–π and π*–d emissions are observable and the latter one appears as a shoulder at *ca.* 670 nm. However, the conjugated main chain emission disappears when the ruthenium content is further increased. This interesting phenomenon was further studied by measuring their excitation spectra at different wavelengths. At 525 nm, the excitation spectra of polymers **1a** and **1d** resemble their main chain absorption band. No observable peak was found in polymer **1e** [Fig. 4(a)]. This indicates the complete quenching of the π*–π emission by the ruthenium complex. At 720 nm, no emission was observed in polymer **1a**. On the other hand, the emission of polymer **1e** at this wavelength originates from both the LC and main chain π–π* electronic transitions [Fig. 4(b)]. These results suggest an energy transfer process in which the emission from the main chain is quenched by the metal complexes. These observations also agree with other ruthenium-containing polymers with a poly(*p*-phenylene) main chain.[19] For those polymers with lower ruthenium content, the metal complex only partially quenches the emission from the conjugated main chain. As a result, emission can be observed at both wavelengths. Similar phenomena were observed in polymers **2a–f** (Fig. 5) and the quenching process is more prominent because the emission bands due to the polymer main chain and metal complex are well-separated. The arrows in Fig. 5 indicate the trend of the emission peaks when the rhenium content is increased.

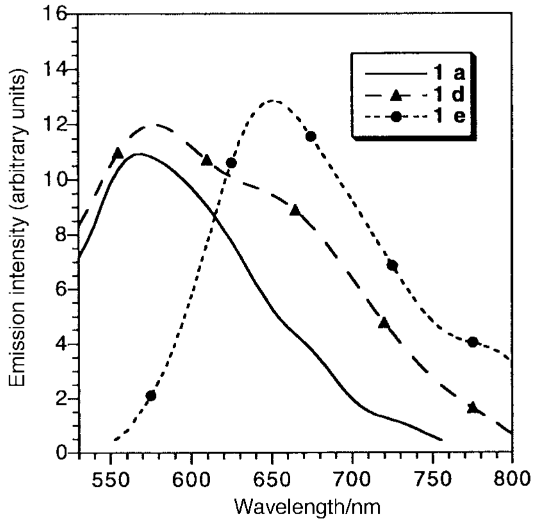


Fig. 3 PL spectra of polymers **1a**, **1d–e**.

Cyclic voltammetry

The cyclic voltammograms of some polymers are shown in Fig. 6. Polymer **1a** shows a reversible, one electron reduction process at $E_{1/2} = -1.0$ V which corresponds to the n-type doping and undoping. After the introduction of ruthenium complexes, the redox processes become more complicated. In all ruthenium-containing polymers it was found that there are several reduction processes which are irreversible. These represent the dipyridophenazine ligand reduction and other n-

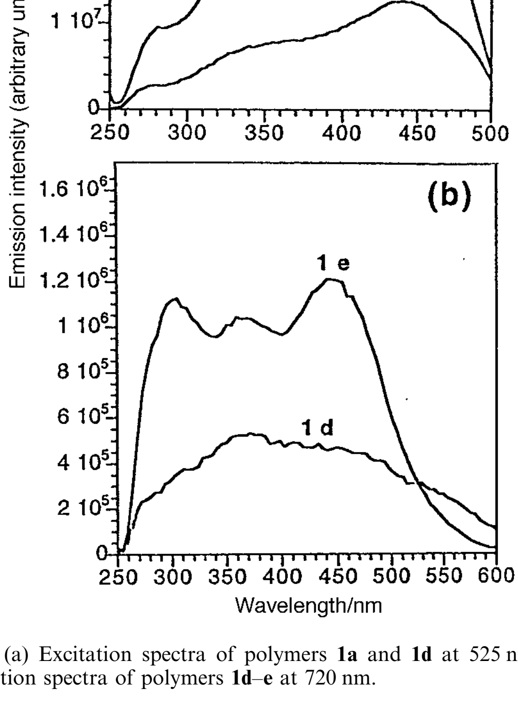


Fig. 4 (a) Excitation spectra of polymers **1a** and **1d** at 525 nm. (b) Excitation spectra of polymers **1d–e** at 720 nm.

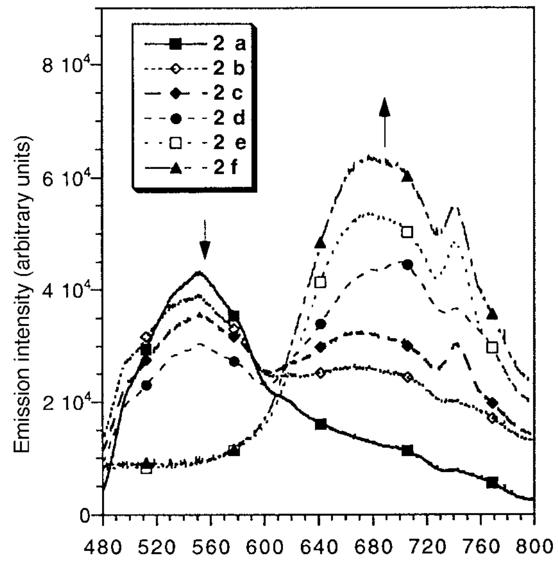


Fig. 5 PL spectra of polymers **2a–f**. The arrows indicate the trend of increasing the rhenium complex content.

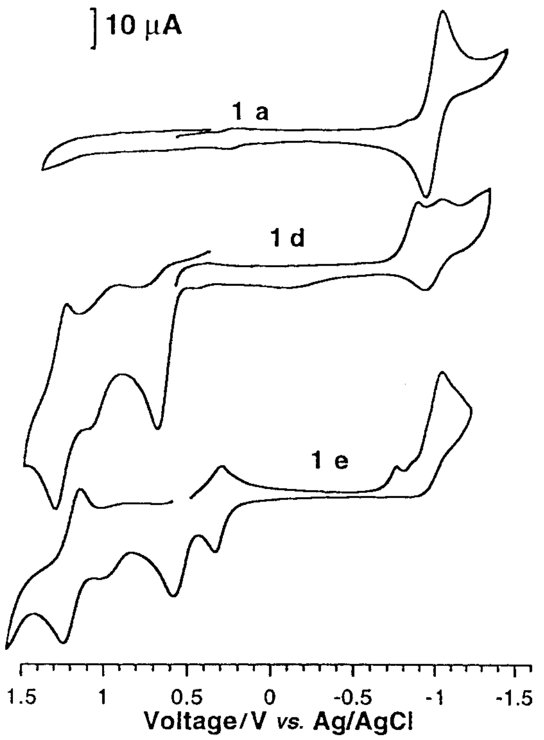


Fig. 6 Cyclic voltammograms of polymers **1a**, **1d–e** in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. Glassy carbon was used as the working electrode, and the scan rate was 50 mV s^{-1}. The redox process at 0.3 V is due to the internal ferrocene standard.

type doping processes. In the reverse scan, the undoping process corresponding to the removal of an electron is observed at 0.7 V. A quasi-reversible oxidation process can be found at 1.2 V. When scanned at a different rate, a similar voltammogram was observed. With reference to the known electrochemical properties of the related $[\mathrm{Ru(bpy)_3}]^{2+}$, the oxidation couple was assigned to the metal-centered Ru(II)→Ru(III) oxidation, while the first reduction to the ligand-centered N–N→N–N$^-$ reduction process. Oxidation involves removal of an electron from the dπ orbital on Ru(II) and reduction involves addition of an electron to the π^* orbital on the bipyridine ligand. The extra anodic peaks may originate from the successive undoping processes. The irreversibility of these redox processes may be due to charge trapping which was also observed in other metal containing conjugated polymers.[15] The electrochemical activities of these polymer–metal complexes may contribute to the charge transport processes by providing more charge carriers in the system.

Light emitting properties

Different ruthenium polymers were fabricated to light emitting diodes (LEDs) ITO/polymer/Al which were subjected to forward bias using a dc power supply. The current–voltage and luminescence–voltage characteristics of the device were measured by applying a dc voltage across the device with the ITO electrode being positive and the aluminium electrode being negative. Fig. 7 shows a typical *I–V* curve for the LED fabricated from polymer **1d**. The thresholds of electroluminescence emission in this device are approximately 10 V. When the voltage was further increased, red light emission was observed. The external quantum efficiency of the device is estimated to be 0.6%. It has been proposed that some ruthenium polypyridine complexes exhibit light emission by the electrochemically generated Ru(III)/Ru(I) which may provide enhancement to the performance of the light emitting device.[20,21] Such electrochemical light emission is characterized by a long charging time. In our devices, a very short response time of the order of milliseconds was observed, which implies the light emission processes are electronic in nature.

Fig. 8 represents the EL spectra of some ruthenium containing polymers. The EL spectral features resemble those of the PL spectra, indicating similar origin of light emission. Polymer **1a** exhibits an emission band centered at *ca.* 550 nm due to the emission from the π^*–π transitions resulting from the recombination of the exciton states. For polymer **1d**, an additional emission band is observed at 630 nm which is interpreted to be the emission from MLCT states [π^*-d (Ru) transitions]. It is also interesting to notice that polymer **1e** only has one emission peak originating from the metal complexes. We postulate that the exciton states were formed through the recombination of oppositely charged polarons generated by the injection of electrons and holes. The light emission can undergo either π^*–π or π^*–d transitions, depending on the composition of the polymers. When the metal content is very high, the π^*–d (Ru) transitions becomes dominant. As a result, only one emission band is observed in polymer **1e** due to its high ruthenium concentration.

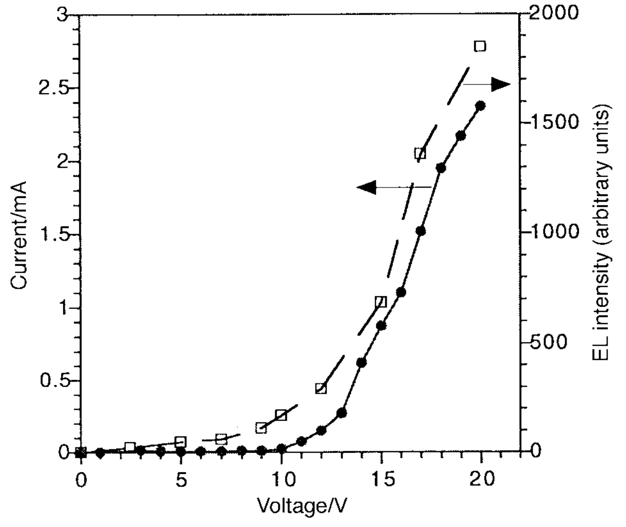


Fig. 7 A plot of current–voltage and luminescence–voltage characteristic for the light emitting device ITO/polymer **1d**/Al.

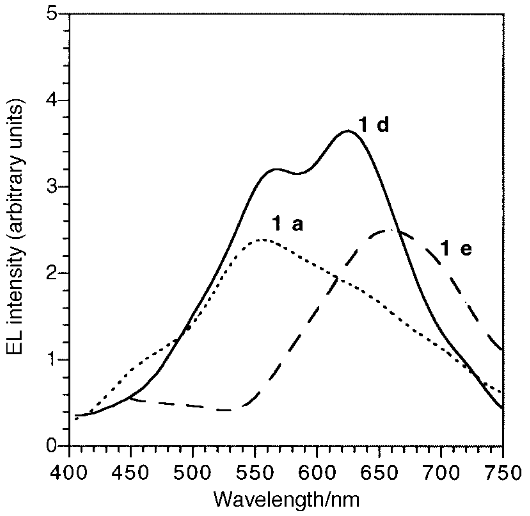


Fig. 8 Electroluminescence spectra of the ruthenium containing polymers **1a**, **1d,e**.

Charge transport properties

The charge transport properties of the polymers were studied by the conventional time-of-flight (TOF) method. It is of fundamental interest to understand the charge migration in the polymer, which can help us to design materials with higher charge carrier mobility and hence better EL performance. Experimental results show that the charge transport process is dispersive in nature with a non-Gaussian distribution.[22,23] Drift mobility μ was calculated according to the equation $\mu = L/t_T E$ where L is the film thickness, t_T is the transit time, and E is the applied electric field. The transit time t_T is the time when the leading part of the carrier distribution reaches the collecting electrode.

Both the electron and hole drift mobilities of the ruthenium containing polymers have been studied and the results are summarized in Table 1. Fig. 9 shows the log μ *vs.* $E^{1/2}$ plot at $T = 298$ K. The plot shows a linear relationship with negative slopes. These interesting phenomena are explained by the presence of off-diagonal disorder in the hopping sites. There are enhanced routes for charge transport involving some short hops not in the direction of the applied field.[24] The electron carrier mobility μ_e of the polymers are in general higher than the hole mobility μ_h, which is in accordance with the reports that quinoxaline typed polymers are n-type semiconducting polymers.[25] In addition, the electron and hole mobilities of polymer **1e** are approximately one order of magnitude higher than those of polymer **1a**. This is attributable to the presence of ruthenium complex which plays an important role as charge carrier. This has been demonstrated in our previous examples of metal containing conjugated polymers. Fig. 10 shows the Arrhenius plot of temperature dependence of hole carrier mobility of polymer **1d** under different electric fields. The graph indicated a thermally activated charge transport process and the activation energy is estimated to be 0.15 eV. This value is lower than those of some phenyl-substituted PPVs[26] or aromatic amine-doped polycarbonates.[27]

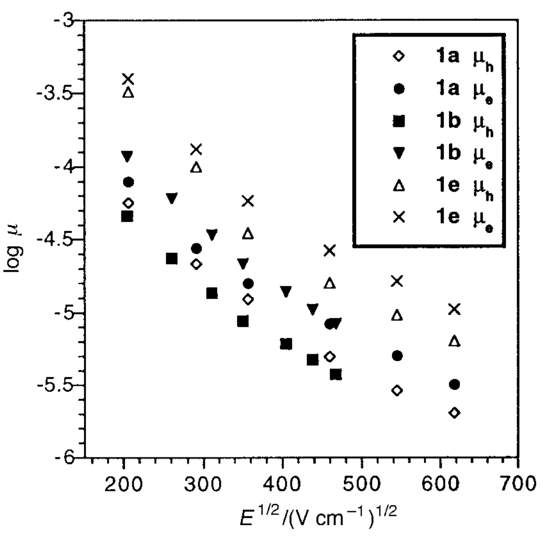


Fig. 9 Electric field dependence electron and hole mobilities for polymers **1a,b**, and **1e** at $T = 298$ K.

Conclusions

We have synthesized two series of conjugated poly(*p*-phenylenevinylene)s functionalized with rhenium or ruthenium dipyridophenazine complexes. The luminescent properties of the polymers strongly depend on the metal complex content. An energy transfer process between the polymer main chain and the metal complex is proposed. In addition, the metal complexes can also serve as charge hopping sites which enhance the charge carrier mobilities. The polymers were fabricated into simple single layer light emitting diodes exhibiting light emission at 550–650 nm under forward bias. This design approach demonstrates the feasibilities of using different transition metals for opto-electronic applications and the physical properties of the polymers can be fine tuned by modifying the metal center.

Experimental

Materials

N-Methylpyrrolidin-2-one (NMP) and *N*,*N*-dimethylformaldehyde (DMF) were distilled over calcium hydride under reduced pressure. Palladium(II) acetate, tri-(*o*-tolyl) phosphine, and pentacarbonylrhenium(I) chloride were purchased from Strem Chemicals Inc. and were used as received. *cis*-Dichlorobis(2,2′-bipyridine)ruthenium dihydrate [*cis*-Ru(bpy)$_2$Cl$_2$·2H$_2$O] (bpy = 2,2′-bipyridine),[28] 5,8-dibromo-2,3-dihexylquinoxaline, 6,9-dibromodipyrido[3,2-*a*:2′,3′-*c*]phenazine, 1,4-divinylbenzene,[29] and monomer **4** were synthesized according to the literature procedures.[19]

Instruments

^{1}H and ^{13}C NMR spectra were collected on a Bruker 300 DPX NMR spectrometer. FTIR spectra (KBr pellet) were collected on a Bio-Rad FTS-7 FTIR spectrometer. Mass

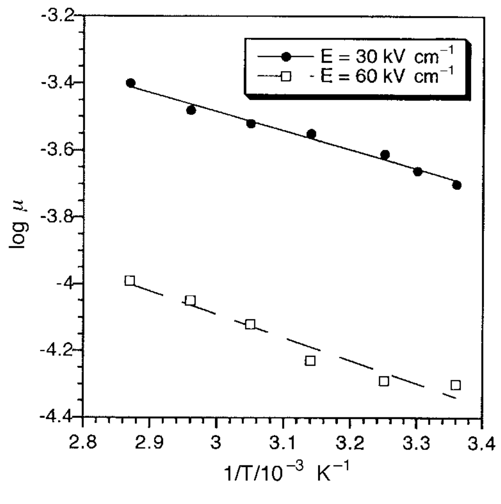


Fig. 10 An Arrhenius plot for the hole mobility of polymer **1d** under different applied electric fields.

spectrometry was performed on a high resolution Finnigan MAT-95 mass spectrometer. UV–VIS spectra were collected on a HP 8452 UV-vis spectrometer. Cyclic voltammetry measurements on polymers were performed on a Princeton Applied Research 270 potentiostat with a glassy carbon working electrode and silver/silver chloride reference electrode. Distilled acetonitrile was used as the solvent and tetrabutylammonium hexafluorophosphate as the supporting electrolyte. A small amount of ferrocene was added as an internal standard. Thermal analyses were performed on a Perkin Elmer TGA7 thermal analyzer with a heating rate of 10 and 15 °C min^{-1}, respectively. The viscosity measurements were performed in a constant temperature bath (30 °C) using an Ubbelohde viscometer, with the solution concentration of 0.25 g dL^{-1} in formic acid or NMP.

Rhenium Complex 5

Under a nitrogen atmosphere, a mixture of 6,9-dibromodipyrido[3,2-*a*:2′,3′-*c*]phenazine (0.13 g, 0.30 mmol) and pentacarbonylrhenium chloride (0.1 g, 0.28 mmol) in toluene (100 mL) was heated at reflux for 2 hours. After cooling, the brown solid was filtered, washed with toluene and diethyl ether, and then dried *in vacuo* (0.14 g, 62%). ^{1}H NMR (CDCl$_3$, 300 MHz) $\delta = 8.09$ (d, 2 H, $J = 5.2$ Hz), 8.18 (s, 2H), 9.51 (d, 2 H, $J = 5.2$ Hz), 9.90 (d, 2 H, $J = 8.2$ Hz); ^{13}C NMR (CDCl$_3$, 75 MHz) $\delta = 124.5$, 125.3, 127.3, 128.3, 129.1, 129.8, 135.4, 136.5, 140.1, 141.1, 155.1; IR (KBr), 2023 (C=O), 1924 (C=O), 1899 (C=O), 1486 (C=N) cm^{-1}; UV-VIS (CHCl$_3$) $\lambda_{\max} = 254$ ($\varepsilon = 3.43 \times 10^4$), 306 ($4.54 \times 10^4$), 372 ($1.18 \times 10^4$ dm^3 mol^{-1} cm^{-1}); MS (FAB): *m*/*z*: 746 (M$^+$), 711 (M$^+$-Cl).

Synthesis of polymers

The synthesis of polymer **1d** is described as the general procedure. A mixture of 5,8-dibromo-2,3-dihexylquinoxaline **6** (0.123 g, 0.269 mmol), 1,4-divinylbenzene **7** (0.07 g, 0.538 mmol), monomer **4** (0.308 g, 0.269 mmol), palladium(II) acetate (6 mg, 5 mol%), and tri-*o*-tolylphosphine (65 mg, 0.4 equiv.) were added to a 25 mL round bottomed flask under a nitrogen atmosphere. DMF (10 mL) was added and the solution was stirred until all the solid dissolved. Tri-*n*-butylamine (0.4 mL) was added and the resulting mixture was heated at 100 °C for 7 days. The polymer was precipitated by pouring the mixture into excess diethyl ether (100 mL) and was collected as a dark brown solid.

The rhenium containing polymers **2a–f** were synthesized by using the same procedures, except that monomer **5** and *m*-cresol were used as solvent for the reaction.

Physical characterizations

The polymer film for time-of-flight was prepared by casting a filtered polymer solution (10 mg mL^{-1} in DMF) onto an ITO glass and the solvent was evaporated slowly. Typical thickness of the polymer film was approximately 1 μm. The polymer film surface was coated with a thin layer of gold electrode (120 Å) by vacuum deposition. The transient photocurrent is generated by a pulse nitrogen laser (wavelength = 337.1 nm, pulse energy = 120 μJ, and pulse width = 3 ns) and was recorded by an HP 54522A digitized oscilloscope. For the fabrication of the light emitting devices, the polymer thin film was prepared by spin coating onto ITO glass slide with a typical thickness of 80–100 nm. A layer of aluminium electrode (thickness = 100 nm) was coated on the polymer film surface by vacuum deposition under a pressure of 10^{-6} mbar. A forward bias was applied to the light emitting diode with a dc power supply and the current–voltage characteristics was studied by a Keithley 2400 autoranging sourcemeter. The photoluminescence (PL) and electroluminescence (EL) spectra of the polymers were collected on a ORIEL MS-257 monochromator equipped with a photomultiplier and an ANDOR DV420-BV charge-coupled device (CCD) detector.

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